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BLEACH ACTIVATOR COMPRISING ALKYLOXY COMPOUND,  
MANUFACTURING METHOD THEREOF AND BLEACHING COMPOSITION  
CONTAINING THE SAME

### Abstract:

#### Abstract of WO2005100530

The present invention relates to a bleaching activator comprising alkyloxy compound, manufacturing method of the bleaching activator and a bleaching composition comprising the bleaching a 109d ctivator. The alkyloxy bleach activator of the present invention is comprised of a granular particle formed by binding a plurality of fine powders composed of alkyloxy compound for bleaching activation with the use of a water-soluble binder, and a coating layer formed on the granular particle. As the coating layer prevents the bleach activator from contacting with inorganic peroxides and moisture in the air, the alkyloxy bleach activator has excellent stability for storage even under the condition of high temperature and humidity when the bleach activator is mixed in oxygen bleaching composition comprising inorganic peroxide. Data supplied from the esp@cenet database - Worldwide

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**WO 2005/100530 A1**

(54) Title: **BLEACH ACTIVATOR COMPRISING ALKYL OXY COMPOUND, MANUFACTURING METHOD THEREOF AND BLEACHING COMPOSITION CONTAINING THE SAME**

(57) Abstract: The present invention relates to a bleaching activator comprising alkyl oxy compound, manufacturing method of the bleaching activator and a bleaching composition comprising the bleaching activator. The alkyl oxy bleach activator of the present invention is comprised of a granular particle formed by binding a plurality of fine powders composed of alkyl oxy compound for bleaching activation with the use of a water-soluble binder, and a coating layer formed on the granular particle. As the coating layer prevents the bleach activator from contacting with inorganic peroxides and moisture in the air, the alkyl oxy bleach activator has excellent stability for storage even under the condition of high temperature and humidity when the bleach activator is mixed in oxygen bleaching composition comprising inorganic peroxide.

**BLEACH ACTIVATOR COMPRISING ALKYL OXY COMPOUND,  
MANUFACTURING METHOD THEREOF AND BLEACHING  
COMPOSITION CONTAINING THE SAME**

5    **TECHNICAL FIELD**

The present invention relates to a bleaching activator comprising alkyl oxy compound, manufacturing method of the bleaching activator, and a bleaching composition containing the bleaching activator.

10   **BACKGROUND ART**

The bleaching method using inorganic peroxides such as sodium perborate tetrahydrate, sodium perborate monohydrate, sodium percarbonate, urea peroxide hydrate, and sodium peroxide enables to remove contaminants more effectively, i.e., stains from fruit juice, coffee, wine, or grass. However, the bleaching ability of the inorganic peroxide significantly varies depending on the temperature. For example, sodium perborate shows optimum effects at a temperature of higher than 80°C, and sodium percarbonate at higher than 60°C, but does not in the cool water used at a temperature range of 20 to 25°C in summer or at about 5°C in winter. Thus, bleach activator method was introduced for inorganic peroxides to present comparable bleaching effects even at a low temperature

Even though TAED (tetra acetyl ethylene diamine) is most commonly used for the compound for activation of bleaching, it is not as effective in removing oily stains such as sebum and blood. US 4,412,934, US 4,483,778, US 4,606,838 and US 4,671,891 disclose bleaching agents using acyl compound as a bleach activator, but it is not cost effective because it requires relatively greater consumption. And US 4,686,061, US 5,043,089 and EP 0210674 disclose carbonate derivatives bleach

activator, but it produces bleach odor as molecular structure changes in laundry water. Moreover US 4,179,390, US 4,259,201, US 5,098,598, US 5,520,844, and US 5,575,947 disclose many organic peroxy-carboxylic acids as bleach activators used in detergent, but these bleach activators are unstable in heat and thus tends to show instability for storage due to loss of active oxygen in itself.

With the reasons above, alkyloxy bleach activator is preferred as it is capable of releasing peroxy-carboxylic acid at low temperature, has excellent bleaching power against hydrophobic stains as well as hydrophilic stains, and rarely makes bleach odor.

Bleach activator, which is generally formed as fine powder less than 100 $\mu$ m, is added to oxygen bleach composition containing inorganic peroxides. In such case, there are some problems of instability for storage promoted by air moisture as both inorganic peroxide and alkyloxy bleach activator are contacted each other in bleaching composition. In particular, this problem becomes more severe under the condition of high temperature and humidity.

#### DISCLOSURE OF INVENTION

The present invention is designed to solve the problems of the prior art, and an object of the present invention is to provide an alkyloxy bleach activator with excellent stability for storage even under the condition of high temperature and humidity when the alkyloxy bleach activator is mixed in oxygen bleach composition containing inorganic peroxides.

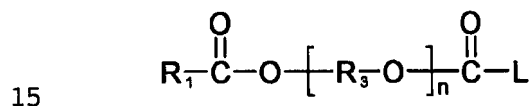
It is another object of the present invention to provide an oxygen bleaching composition, which has excellent stability for storage, containing the alkyloxy bleach activator.

Moreover, it is another object to provide a manufacturing method of the bleach activator composed of uniform-sized granular particles without decreasing

the effective component of the bleach activator.

To achieve the technical objectives, alkyloxy bleach activator of the present invention is comprised of granular particle formed by binding of a plurality of fine powders composed of alkyloxy compound for bleaching activation with the use of a water-soluble binder, as shown in the following Chemical Formula 1, and a coating layer formed on a surface of the granular particle. As the coating layer prevents the bleach activator from being exposed to inorganic peroxides and moisture in the air, the alkyloxy bleach activator has excellent stability for storage even under the condition of high temperature and humidity when the bleach activator is mixed in oxygen bleaching composition containing inorganic peroxide.

#### Chemical Formula 1

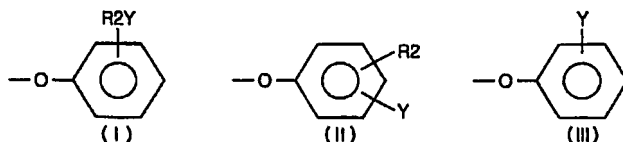


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where  $R_1$  and  $R_3$  are respectively one selected from the group consisting of alkyl, alkylene, aryl, alkaryl, and alkarylene, which have a carbon number of 1 to 20,  $n$  is an integer from 0 to 10, and  $L$  is a leaving group selected from the group consisting of (I) to (III) of the following Chemical Formula 2:

20

#### Chemical Formula 2



25

where  $R_2$  is one of alkyl and alkylene, having a carbon number of 1 to 20,  $Y$  is one selected from the group consisting of hydrogen, chlorine, bromine,  $SO_3M$ ,

CO<sub>2</sub>M and OSO<sub>2</sub>M, and M is one selected from the group consisting of hydrogen, alkali metal ion, ammonium ion and equivalent alkaline earth metal.

Preferably, the alkyloxy bleach activator of the present invention is produced in spherical or cylindrical shape.

5           The spherical alkyloxy bleach activator is produced by a method comprising; (S1) forming a fine powder fluidized bed by putting a plurality of fine powders composed of alkyloxy compound for bleaching activation expressed by the Chemical Formula 1 into a predetermined container where gas flows, and then fluidizing the fine powders; (S2) binding the fine powders to each other by spraying  
10 a solution in which a water-soluble binder is dissolved to the fine powders so that the fine powders are formed into a plurality of spherical granular particles having an average diameter of 0.1 to 4 mm; and (S3) forming a coating layer on the spherical granular particle by spraying a solution containing a coating material to a fluidized bed composed of a plurality of the formed spherical granular particles. By this  
15 method, the spherical bleach activator with uniform size and shape can be obtained, while effective component of the bleach activator is not largely decreased.

Moreover, the cylindrical alkyloxy bleach activator of the present invention is produced by a method comprising; (S1) mixing a plurality of fine powders composed of alkyloxy compound for bleaching activation expressed by the  
20 following Chemical Formula 1 with a water-soluble binder, and making the mixture into cylindrical granular particles having an average diameter of 0.1 to 3 mm and a length of 0.1 to 30 mm with the use of an extruder and a pelletizer; (S2) forming a cylindrical granular particle fluidized bed by putting cylindrical granular particles into a predetermined container where a gas flows, and then fluidizing the particles;  
25 and (S3) forming a coating layer on a surface of the cylindrical granular particle by spraying a solution containing a coating material to the cylindrical granular particle fluidized bed. By this method, the cylindrical bleach activator with uniform size

and shape can be obtained, while effective component of the bleach activator is not largely decreased, and its productivity is very high.

And the present invention provides a bleach composition containing inorganic peroxides, which includes 0.01 to 15wt% of the alkyloxy bleach activator on the basis of the weight of the entire composition. This bleach composition has excellent stability for storage even under the condition of high temperature and humidity, thus bleaching, washing, and sterilizing abilities effectively last for a longer period of time.

#### 10 BEST MODES FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention will be described in more details.

The alkyloxy bleach activator of the present invention is comprised of: a granular particle formed by binding a plurality of fine powders composed of alkyloxy compound for bleaching activation expressed by the Chemical Formula 1 mentioned above with the use of a water-soluble binder; and a coating layer formed on a surface of the granular particle.

The alkyloxy compound for bleaching activation expressed by the chemical formula 1 is capable of releasing peroxycarboxylic acid even at a low temperature, having excellent bleaching effect for hydrophobic stains as well as hydrophilic stains, and hardly generating bleach odor. Commonly the compound is produced in forms of fine powder less than 100 $\mu$ m. The alkyloxy compound for bleaching activation may be obtained by the method disclosed in US 5,705,091, or by the reaction of chloroformate with hydroxybenzene, its derivatives, or its salt in solvent. The chloroformate is made by the reaction of fatty acid monoester with phosgene, diphosgene or triphosgene under basic condition.

A plurality of fine powders composed of the alkyloxy compound are bound by a water-soluble binder to form, for example, spherical granular particles with an

average diameter of 0.1 to 4mm or cylindrical granular particles with an average diameter of 0.1 to 3mm and a length of 0.1 to 30mm. The spherical or cylindrical granular particle mentioned above allows the coating layer to be easily formed on the surface, and improves stability for storage as its exposure to inorganic peroxide and moisture in the air relatively decreases. Any component, if it is soluble easily in the laundry water and capable of binding fine powders to each other, can be used as the water-soluble binder. For example, white sugar, glucose, starch, gelatin, polyethylene glycol, alkyl polyethoxylate, sorbitan fatty acid esters, linear alkylbenzene sulfonate, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, hydroxypropyl cellulose, arabic gum, ethyl cellulose and polyvinyl pyrrolidone, can be used alone or by mixture. Preferably, 0.5 to 10wt% of water-soluble binder is recommended on the basis of the entire weight of the granular particles in case of the spherical granular particles, while 0.5 to 20wt% in case of the cylindrical granular particles, in order to give sufficient binding effect and maintain the content of alkyloxy compound for bleaching activation more than a certain criteria.

The granular particle, formed as mentioned above, shows improved stability for storage to some extent when it is mixed with oxygen bleach composition, but not as effective particularly under the condition of high temperature and humidity because inorganic peroxide and bleach activator still contact each other in the bleaching composition, thereby deteriorating stability as moisture in the air facilitates the reaction between them.

To solve these problems, the bleach activator of the present invention has a coating layer on a surface of the granular particle. The coating layer significantly improves stability for storage since it prevents fine powders from contacting with inorganic peroxide and moisture in the air. As a coating material, inorganic substance, water-soluble organic substance or mixture of them can be used if it can



be easily eliminated from the surface of the granular particle by solvating or dispersing in the laundry water. For example, but not limited herein, the inorganic substance is at least one selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, sodium sulfate, zeolite, talc, clay, and silica, and the water-soluble organic substance is at least one selected from the group consisting of polyethylene glycol, alkyl polyethoxylate, carboxy methyl cellulose, hydroxyethyl cellulose, methyl cellulose, hydroxypropyl cellulose, 2-methyl-5-vinylpyridine-methylacrylate-methacrylic acid polymer, and polyvinyl pyrrolidone. Particularly, in order to ensure both hardness of the coating layer and facility of eliminating the coating layer, the coating layer is preferably made of mixture of inorganic and water-soluble organic substances, with ideal ratio of about 1:10 to 10:1 wt%. The thickness of the coating layer should be about 1 to 100 $\mu$ m or more preferably about 5 to 25 $\mu$ m.

Hereinafter, the manufacturing method of alkyloxy bleach activator of the present invention will be described in more details.

Mixer is commonly used to make fine powders into granular particles, herein binder is used to bind fine powders to each other. But, this method has drawbacks that the content of effective components is largely decreased and the granular particles are not uniform in size and shape since the mixer requires a large amount of binder.

In order to reduce these drawbacks, in the present invention we obtained spherical granular particles by fluidizing fine powders comprising of alkyloxy compound for bleaching activation and then spraying the solution of water-soluble binder thereto, or obtained cylindrical granular particles with the use of an extruder and a pelletizer.

A manufacturing process of the spherical granular particles is as follows.

Fine powders of the alkyloxy compound expressed by the chemical formula

1 are put into a predetermined container where gas flows and then fluidized to form a fine powder fluidized bed. In the fluidized bed, fine powders are in a state of fluidization where they can be easily fluidized like boiling liquid because fluidized resistance equals gravity.

5        Thereafter, the fine powders are bound to each other just by spraying a solution of water-soluble binder dissolved in water or organic solvent into the fluidized bed. In such case, suitable heat air is given into the fluidized bed in order to evaporate the solvent contained in the bound fine powders. Herein, to produce spherical granular particles with average diameter of 0.1 to 4mm, the  
10       concentration of the binder and spraying rate of the solution are controlled. As seen above, if the granular particles are formed in the fluidized bed, a higher content of effective component of fine powders as well as uniform shape and size of the granular particles is achieved because even a small amount of binder resin could provide sufficient binding ability between the fine powders.

15       Moreover, a manufacturing process of the cylindrical granular particles is as follows.

      Cylindrical granular particles of the fine powders are obtained with the use of an extruder and a pelletizer. Namely, in order to produce the cylindrical granular particles having an average diameter of 0.1 to 3 mm and a length of 0.1 to  
20       30 mm, a plurality of fine powders composed of alkyloxy compound for bleaching activation are mixed with a water-soluble binder in an extruder and a pelletizer, and then extruded or molded.

      By this method, the bleach activator comprising cylindrical granular particles with uniform size and shape can be obtained, while effective component of  
25       the bleach activator is not largely decreased, and its productivity is very high.

      Next step is to form a coating layer on the surface of the granular particles by spraying the solution in which coating materials are dissolved or dispersed into

the fluidized bed composed of the spherical or cylindrical granular particles produced by above process. In this case, suitable heat air is given into the fluidized bed in order to evaporate the solvent contained in the coating layer.

As for the method for manufacturing alkyloxy bleach activator according to the present invention, kind or content of the water-soluble binder and the coating materials used is the same as described above.

The alkyloxy bleach activator of the present invention is added to oxygen bleaching composition containing inorganic peroxide when used. Considering an activation effect to peroxide and a dissolving rate, the content of the bleach activator is preferably 0.01 to 15wt% on the basis of the total weight of the entire composition. If the content of it is less than 0.01wt%, the inorganic peroxide may not be sufficiently activated. If the content of it is more than 15wt%, the inorganic peroxide may be activated too rapid.

As for the peroxide, organic peroxyacid and inorganic compound generating hydrogen peroxide such as percarbonate salt ( $M_2C_2O_6$ ), perborate salt ( $MBO_3$ ), perphosphate salt, persulfate salt and urea peroxide are generally used for the oxygen bleaching composition. Among them, percarbonate salt, perborate salt and their mixture are suitable for the peroxide in the present invention. In particular, considering bleaching effects and economic merits, the content of the inorganic peroxide is preferably 1 to 80wt% out of the total weight of the composition.

When making the bleaching composition containing inorganic peroxide according to the present invention, components except the inorganic peroxide and the bleach activator are commonly selected and suitably mixed according to the kind and usage thereof. Now, surfactant and builder, which may be added to the bleaching composition according to the present invention, are described.

As for the surfactant, anion surfactant or nonion surfactant may be used. The content of the surfactant is not specially limited, but preferably 1 to 40wt% out of

the total weight of the composition. The anion surfactant may adopt alkylbenzene sulfonate (ABS), fatty acid salt, alkyl monosulfonate, alphaolefin sulfonate (AOS) and so on. The nonion surfactant may adopt oxoalcohol polyethylene glycol, fatty acid polyoxyethylene glycol, alkylphenyl polyoxyethylene glycol, or  
5 polyoxyethylene glycol, and so on.

In addition, the builder is an alkali metal salt additive for improving washing ability of the surfactant. For example, the builder may adopt polyphosphate alkali metal salt such as sodium tripolyphosphate; alumino silicate such as zeolite; polyacetal carboxylate; polycarboxylate; carbonates such as sodium carbonate  
10 ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ); silicates such as layered crystalline  $\alpha\text{-Na}_2\text{SiO}_3$  or  $\beta\text{-Na}_2\text{SiO}_3$ ; and so on. A content of the builder is preferably 10 to 50wt% on the basis of the total weight of the composition in consideration of improvement of the washing ability of the surfactant.

In addition to the above substances, the oxygen bleaching composition of the  
15 present invention may further include other additives which are commonly used for the detergent, for example, inorganic salts such as sodium carbonate and sodium sulfonate, fluorescent dyes, enzymes, perfume and so on.

Hereinafter, the present invention will be described in more details. However, it should be understood that the detailed description and specific examples, while  
20 indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

## 25 The manufacturing process of spherical granular particles.

### Manufacturing examples 1-1 and 1-2

The fine powders of OCECB(octyl-carboxyl-ethoxy-carboxyl-

benzenesulfonate) as alkyloxy compound for bleaching activation were put into a fluidization device (GLATT company, GPCG), and then fluidized them to form a fluidized bed. Aqueous solution of starch was sprayed into the fluidized bed, heat air is blown into the fluidized bed to evaporate the solvent suitably, thereby making spherical granular particles having an average diameter of 1mm.

Processing condition and composition of the spherical granular particle are shown in table 1.

Table 1

Manufacturing example No.	1-1	1-2
OCECB (wt%)	95	90
Starch (wt%)	2	5
Water (wt%)	3	5
Injection temp. of solution (°C)	60	60
Pressure of spraying (kgf/cm <sup>2</sup> )	1.0	1.0
Inlet temp. (°C)	85	85
Outlet temp. (°C)	42	42
Spraying Rate (g/min)	9.0~11.5	9.0~11.5

10

The manufacturing process of cylindrical granular particles.

Manufacturing examples 2-1 and 2-2

The fine powders of OCECB(octyl-carboxyl-ethoxy-carboxyl-benzenesulfonate), what is alkyloxy compound for bleaching activation, and polyoxyalkylether, what is a binder were put into an extruder in the ratio of table 2 as below, mixed, extruded through a spherical hole and cut off by suitable length. The cylindrical granular particles have a diameter of 1.0mm and a length of 2.0mm. Rotational frequency of the extruder used and composition of the cylindrical granular particle are shown in table 2.

20

Table 2

Manufacturing example No.	2-1	2-2
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OCECB(wt%)	96	95
Polyoxyethylene alkyl ether (wt%)	4	5
Rotational frequency(rpm)	60	90

The coating process of spherical granular particles.

Manufacturing examples 3-1 to 3-4

The coating process was performed in the fluidized bed composed of the spherical granular particles produced by the method as described above, using each one or mixture of polyethylene glycol, sodium sulfate, and zeolite according to the table 3. 600g of the spherical granular particles produced by the manufacturing example 1 was put into the container of the fluidization device, and fluidized with heat air. The solution of coating material, consisting of each one or mixture of any of polyethylene glycol, sodium sulfate, and zeolite as described in table 3, was sprayed through a spray nozzle equipped at lower end of the container into the fluidized bed. Then, the coating layer was formed. Processing condition and composition of the coated bleach activators are shown in table 3 as below. The content of each coating material is expressed by wt% of each component used on the basis of the total weight of the entire composition.

Table 3

Manufacturing example No.	3-1	3-2	3-3	3-4
Polyethylene glycol	4	4		4
Sodium sulfate			4	4
Zeolite		4		
Temp. of solution (°C)	60	65	60	65
Thickness of coating layer (μm)	8	20	3	17
Pressure of spraying (kgf/cm <sup>2</sup> )	1.2	1.4	1.4	1.2
Inlet temp. (°C)	85	85	85	85
Outlet temp. (°C)	36	38	40	36
Air flow (m <sup>3</sup> /hr)	45	45	45	45
Spraying Rate (g/min)	9.0~11.5	9.5~13.0	10.0~11.0	10.0~11.5

The coating process of cylindrical granular particles.

Manufacturing examples 4-1 to 4-4

Cylindrical granular particles, obtained by manufacturing example 2, were coated on their according to the following table 4 in the same way as the manufacturing example 3. Processing condition and composition of the coating layer are shown in table 4 as below. The content of each coating material is expressed by wt% in the table 4 on the basis of the total weight of the entire composition.

10 Table 4

Manufacturing example No.	4-1	4-2	4-3	4-4
Polyethylene glycol	4	4		4
Sodium sulfate			4	4
Zeolite		4		
Temp. of solution (°C)	60	65	60	65
Thickness of coating layer ( $\mu\text{m}$ )	7	20	5	15
Pressure of spraying ( $\text{kgf}/\text{cm}^2$ )	1.2	1.4	1.4	1.2
Inlet temp. (°C)	85	85	85	85
Outlet temp. (°C)	36	38	40	36
Air flow ( $\text{m}^3/\text{hr}$ )	45	45	45	45
Spraying Rate (g/min)	9.0~11.5	9.5~13.0	10.0~11.0	10.0~11.5

Test of stability for storage

The active oxygen titrimetry was used as below in order to test stability for storage of the bleaching component in the product in case the bleach activator produced by combination of the manufacturing examples 1 and 3, or 2 and 4 is used as a component of detergent composition. 0.8parts by weight of detergent base (30wt% of surfactant; 20wt% of soda ash; 20wt% of soda silicate; 20wt% of Erigeron Canadensis), 0.2parts by weight of sodium percarbonate, 0.05parts by weight of the bleach activator produced was added to a vial. After it kept in thermohydrostat of 30°C and 80% of relative humidity for 3 or 5 days with the

cover open, the value of residual active oxygen was measured by titration. As for the test of active oxygen, KS method was adopted.

**Table 5**

	Manufacturing example (to form granular particles)	Manufacturing example (to form coating layers)	Detergent (g)	Percarbonate (g)	Bleach activator (g)	Residual active oxygen after 3 days (%)	Residual active oxygen after 5 days (%)
Embodiment 1	1-1	3-1	0.8	0.2	0.05	74	64
Embodiment 2	1-1	3-2	0.8	0.2	0.05	99	87
Embodiment 3	1-1	3-3	0.8	0.2	0.05	71	59
Embodiment 4	1-1	3-4	0.8	0.2	0.05	73	67
Embodiment 5	1-2	3-1	0.8	0.2	0.05	77	66
Embodiment 6	1-2	3-2	0.8	0.2	0.05	97	88
Embodiment 7	1-2	3-3	0.8	0.2	0.05	79	58
Embodiment 8	1-2	3-4	0.8	0.2	0.05	74	61
Embodiment 9	2-1	4-1	0.8	0.2	0.05	76	68
Embodiment 10	2-1	4-2	0.8	0.2	0.05	99	87
Embodiment 11	2-1	4-3	0.8	0.2	0.05	79	67
Embodiment 12	2-1	4-4	0.8	0.2	0.05	73	67
Embodiment 13	2-2	4-1	0.8	0.2	0.05	77	66
Embodiment 14	2-2	4-2	0.8	0.2	0.05	97	88
Embodiment 15	2-2	4-3	0.8	0.2	0.05	79	68
Embodiment 16	2-2	4-4	0.8	0.2	0.05	74	61
Comparative example 1	1-2	-	0.8	0.2	0.05	62	36
Comparative example 2	-	-	0.8	0.2	0.05	62	20
Comparative example 3	2-1	-	0.8	0.2	0.05	62	36

5

Referring to the table 5 as described above, it is found that the bleaching composition comprising the bleach activator of the present invention (embodiments 1~16) shows excellent stability for storage, compared to the comparative examples.

Another bleaching compositions were made as follows on the basis of the previous results. To make the bleaching compositions, components except additives and bleaching components are firstly made into granulated powder, and then the additives and the bleaching components are added to and mixed with the granulated



powder. The unit is wt%.

**Table 6**

Raw material	Embodiment		Comparative example			
	17	18	4	5	6	7
Percarbonate salt	15	15	15	15	15	15
Bleach activator by embodiment 2	5	-	-	-	-	-
Bleach activator by embodiment 10	-	5	-	-	-	-
Bleach activator by comparative example 1	-	-	5	-	-	-
Bleach activator by comparative example 3		-	-	5	-	-
TAED	-	-	-		5	-
LAS	10	10	10	10	10	10
Polyoxyethylene alkyl ether	5	5	5	5	5	5
Alphaolefinsulfonate salt	3	3	3	3	3	3
Sodium carbonate	To 100	To 100	To 100	To 100	To 100	To 100
Sodium sulfate	10	10	10	10	10	10
Zeolite 4A	20	20	20	20	20	20
Fluorescent dye	0.15	0.15	0.15	0.15	0.15	0.15
Enzyme	0.5	0.5	0.5	0.5	0.5	0.5

- 5 In Table 6, TAED is tetra acetyl ethylene diamine, LAS is linear alkylbenzene sulfonate, the fluorescent dye is Tinopal DMA-X (manufactured by Ciba Specialty Chemical Co.), and the enzyme is Savinase 12.0T (manufactured by Novozyme).

10 Then, tests for bleaching ability, washing ability and sterilizing ability of 1kg of the bleaching compositions manufactured by the embodiments 17 and 18, and the comparative examples 4 to 7 were conducted by using the following method after being kept in thermohydrostat of 30°C and 80% of relative humidity for 5 days.

### Experiment for Evaluation in Bleaching Ability

Red wine (EMPA 114), coffee (WFK BC-2), red pepper (WFK 10P) and tea (WFK BC-3) were evenly spread on a white cotton fabric of 8×8 cm<sup>2</sup>, and then dried. The bleaching compositions made in the embodiments 17 and 18, and the comparative examples 4 to 7 are respectively added into a Terg-o-tometer, the washability measurer, at a ratio of 1 g/L together with water at a temperature of 20°C and hardness of 50 CaCO<sub>3</sub> ppm. The cotton fabric is put therein, and then washed for 10 minutes, rinsed for 3 minutes, and naturally dried.

A colorimeter is used to measure whiteness of the cotton fabric both before and after the washing, respectively. Then, a bleaching ability is calculated using Kubelka-Munk's Equation expressed by the following Equation 1. The calculated results are shown in the following Table 7.

### Equation 1

$$\text{bleaching ratio(\%)} = [(1-R_s)^2/2R_s - (1-R_b)^2/2R_b] / [(1-R_s)^2/2R_s - (1-R_o)^2/2R_o] \times 100$$

In Equation 1,  $R_s$  is a surface reflectivity of the cotton fabric when contaminated,  $R_b$  is a surface reflectivity of the cotton fabric after removing contaminants, and  $R_o$  is a surface reflectivity of the white cotton fabric in its original state.

Table 7

	Embodiment		Comparative Examples			
	17	18	4	5	6	7
Red Wine	94%	94%	82%	82%	73%	67%
Coffee	93%	93%	79%	79%	68%	59%

Red Pepper	92%	92%	80%	80%	62%	57%
Tea	92%	92%	76%	76%	73%	61%

Table 7 shows that the bleaching composition manufactured by the embodiments 17 and 18 containing the bleach activator of the present invention presents excellent bleaching ability against contamination of red wind, coffee, red pepper and tea.

#### Test for Evaluation in Washing Ability

The bleaching compositions made in the embodiments 17 and 18, and the comparative examples 4 to 7 are respectively added into a Terg-o-tometer at a ratio of 1 g/L together with water at a temperature of 20°C and hardness of 133CaCO<sub>3</sub> ppm. Two pieces of cotton fabric of 8×8 cm<sup>2</sup> contaminated by WFK 10D and WFK 20D and eight pieces of contaminated fabric provided by Japan Washing Science Association (JWSA) are put therein. They are washed for 10 minutes, rinsed for 3 minutes and naturally dried.

A colorimeter is used to measure whiteness of the fabric both before and after the washing, and then a bleaching ability is calculated using Kubellka-Munk's Equation expressed by Equation 1. The calculated results are shown in the following Table 8.

Table 8

	Embodiments		Comparative Examples			
	17	18	4	5	6	7
WFK 10D	84%	84%	79%	79%	73%	71%
WFK 20D	83%	83%	81%	81%	74%	72%
Contaminated fabric of JWSA	84%	84%	80%	80%	73%	70%

Seeing Table 8, it is found that the bleaching composition manufactured by the embodiments 17 and 18 containing the bleach activator of the present invention shows excellent washing ability against hydrophilic and hydrophobic stains.

5

#### Experiment for Evaluation in Sterilizing Ability

This experiment was conducted using eleven kinds of bacilli, namely *P. aeruginosa*, *E. coli*, *Klebsiella pneumoniae*, *Staphylococcus epidermis*, *Staphylococcus aureus*, *Vibrio parahaemolyticus*, *Shigella flexneri*, *Acineobacter*  
10 *baumannii*, *Aeromonas hydrophyla*, *Enterobacter aerogenes*, and *Salmoella typhimurium*. As for medium, SDC medium composed by adding 30g of Casitone, 5g of Tween-80, 5g of Soyton, 5g of NaCl, 0.7g of Lecithin and 15g of Agar into 1L of water is used.

After preparing 1L of 0.85% sodium chloride solution (20°C) in 6 beakers,  
15 the above-mentioned bacilli are added at the concentration of  $2.0$  to  $5.0 \times 10^5/\text{mL}$  into each beaker and then stirred. And then, the bleaching compositions made in the embodiments 17, 18 and the comparative examples 4 to 7 are respectively added into each beaker at a ratio of 1.0 g/L, and the number of bacilli is measured with the passage of time. At this time, a beaker to which the bleaching composition is not  
20 added is selected as a control group.

1mL of solution is obtained from each beaker, respectively after 15 and 20 minutes since adding the bleaching composition, and then serially diluted using 0.85% NaCl solution as a dilution buffer. After that, the solution is spread to a solid medium and cultivated for 24 hours in an incubator at a temperature of 37°C.  
25 And then, the colony counting is conducted for the embodiments 17, 18, and the comparative examples 4 to 7 together with the control group, and death rates of bacilli are measured for the embodiments 17, 18, and the comparative examples 4 to

7 by comparison with the control group. The result of this experiment is shown in the following Table 9.

**Table 9**

	After 15 minutes						After 20 minutes					
	Embodiments		Comparative examples				Embodiments		Comparative examples			
	17	18	4	5	6	7	17	18	4	5	6	7
<i>P. aeruginosa</i>	99.9	99.9	99.9	99.9	99.9	90.3	99.9	99.9	99.9	99.9	99.9	99.9
<i>E. coli</i>	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
<i>K. pneumoniae</i>	99.9	99.9	99.9	99.9	92.6	82.6	99.9	99.9	99.9	99.9	99.9	99.9
<i>S. epidermis</i>	99.9	99.9	99.9	99.9	96.3	82.5	99.9	99.9	99.9	99.9	99.9	99.9
<i>S. aureus</i>	99.9	99.9	99.9	99.9	90.9	87.6	99.9	99.9	99.9	99.9	99.9	99.9
<i>V. parahaemolyticus</i>	99.9	99.9	99.9	99.9	90.2	82.6	99.9	99.9	99.9	99.9	99.9	99.9
<i>S. flexneri</i>	99.9	99.9	99.9	99.9	93.3	85.4	99.9	99.9	99.9	99.9	99.9	99.9
<i>A. baumannii</i>	99.9	99.9	99.9	99.9	94.5	86.2	99.9	99.9	99.9	99.9	99.9	99.9
<i>A. hydrophyla</i>	99.9	99.9	99.9	99.9	92.3	86.7	99.9	99.9	99.9	99.9	99.9	99.9
<i>E. aerogenes</i>	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
<i>S. typhimurium</i>	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9

5

As shown in Table 9, it is understood that the bleaching composition manufactured by embodiments 17 and 18 containing the bleach activator of the present invention shows excellent initial death rate.

## 10 INDUSTRIAL APPLICABILITY

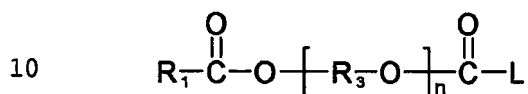
As described above, the alkyloxy bleach activator composed of the granular particle with a coating layer according to the present invention, shows excellent stability for storage when mixed in oxygen bleaching composition containing inorganic peroxide even under the condition of high temperature and humidity. Thus, the bleaching composition is very useful for domestic and industrial use because it provides excellent bleaching ability, washing ability, and sterilizing ability for a long period of time. Moreover, according to the manufacturing method of the present invention, the bleach activator comprising granular particles

with uniform size can be obtained without largely decreasing the effective component of the bleach activator.

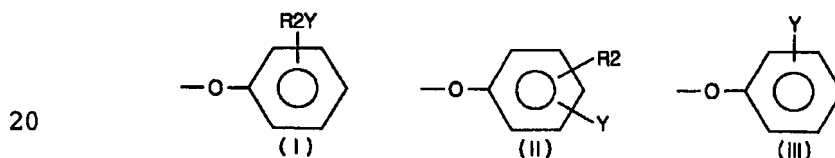
WHAT IS CLAIMED:

1. A bleach activator having alkyloxy compound, comprising:

- (a) a granular particle formed by binding a plurality of fine powders  
 5 composed of alkyloxy compound for bleaching activation expressed by the  
 following Chemical Formula 1 with the use of a water-soluble binder:

Chemical Formula 1

where  $R_1$  and  $R_3$  are respectively one selected from the group consisting of  
 alkyl, alkylene, aryl, alkaryl, and alkarylene, which have a carbon number of 1 to 20,  
 n is an integer from 0 to 10, and L is a leaving group selected from the group  
 15 consisting of (I) to (III) of the following Chemical Formula 2:

Chemical Formula 2

where  $R_2$  is one of alkyl and alkylene, having a carbon number of 1 to 20, Y  
 is one selected from the group consisting of hydrogen, chlorine, bromine,  $SO_3M$ ,  
 $CO_2M$  and  $OSO_2M$ , and M is one selected from the group consisting of hydrogen,  
 25 alkali metal ion, ammonium ion and equivalent alkaline earth metal; and

- (b) a coating layer formed on a surface of the granular particle.

2. A bleach activator having alkyloxy compound according to claim 1,  
wherein the granular particle is spherical with an average diameter of 0.1 to 4mm.
3. A bleach activator having alkyloxy compound according to claim 2,  
5 wherein a content of the water-soluble binder is 0.5 to 10 wt% on the basis  
of the entire weight of the spherical granular particles.
4. A bleach activator having alkyloxy compound according to claim 1,  
wherein the granular particle is cylindrical with an average diameter of 0.1  
10 to 3mm and a length of 0.1 to 30mm.
5. A bleach activator having alkyloxy compound according to claim 4,  
wherein a content of the water-soluble binder is 0.5 to 20 wt% on the basis  
of the entire weight of the cylindrical granular particles.
- 15 6. A bleach activator having alkyloxy compound according to claim 1,  
wherein the water-soluble binder is at least one selected from the group  
consisting of white sugar, glucose, starch, gelatin, polyethylene glycol, alkyl  
polyethoxylate, sorbitan fatty acid esters, linear alkylbenzene sulfonate,  
20 carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, hydroxypropyl  
cellulose, arabic gum, ethyl cellulose and polyvinyl pyrrolidone.
7. A bleach activator having alkyloxy compound according to claim 1,  
wherein the coating layer is formed of one selected from the group  
25 consisting of inorganic substance, water-soluble organic substance, and their  
mixture.



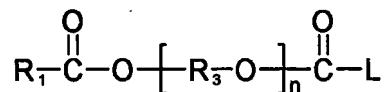
8. A bleach activator having alkyloxy compound according to claim 7,  
 wherein the inorganic substance is at least one selected from the group  
 consisting of sodium carbonate, sodium bicarbonate, potassium carbonate,  
 potassium bicarbonate, sodium sulfate, zeolite, talc, clay, and silica; and wherein the  
 5 water-soluble organic substance is at least one selected from the group consisting of  
 polyethylene glycol, alkyl polyethoxylate, carboxy methyl cellulose, hydroxyethyl  
 cellulose, methyl cellulose, hydroxypropyl cellulose, 2-methyl-5-vinylpyridine-  
 methylacrylate-methacrylic acid polymer, and polyvinyl pyrrolidone.

10 9. A bleach activator having alkyloxy compound according to claim 1,  
 wherein the coating layer has a thickness of 1 to 100  $\mu\text{m}$ .

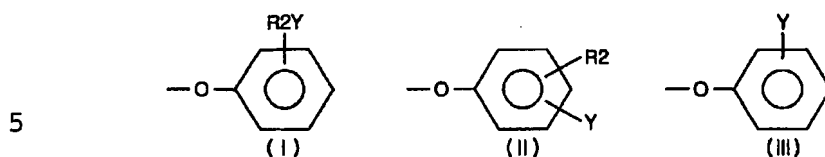
10. A method for manufacturing a bleach activator having alkyloxy  
 compound, comprising:

15 (S1) forming a fine powder fluidized bed by putting a plurality of fine  
 powders composed of alkyloxy compound for bleaching activation expressed by the  
 following Chemical Formula 1 into a predetermined container where a gas flows,  
 and then fluidizing the fine powders:

20 Chemical Formula 1



where  $\text{R}_1$  and  $\text{R}_3$  are respectively one selected from the group consisting of  
 25 alkyl, alkylene, aryl, alkaryl, and alkarylene, which have a carbon number of 1 to 20,  
 $n$  is an integer from 0 to 10, and  $\text{L}$  is a leaving group selected from the group  
 consisting of (I) to (III) of the following Chemical Formula 2:

Chemical Formula 2

where  $R_2$  is one of alkyl and alkylene, having a carbon number of 1 to 20, Y is one selected from the group consisting of hydrogen, chlorine, bromine,  $SO_3M$ ,  $CO_2M$  and  $OSO_2M$ , and M is one selected from the group consisting of hydrogen, alkali metal ion, ammonium ion and equivalent alkaline earth metal; and

10

(S2) binding the fine powders to each other by spraying a solution in which a water-soluble binder is dissolved to the fine powders so that the fine powders are formed into a plurality of spherical granular particles having an average diameter of 0.1 to 4 mm; and

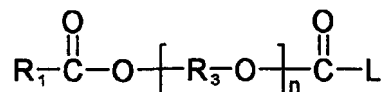
15 (S3) forming a coating layer on a surface of the spherical granular particle by spraying a solution containing a coating material to a fluidized bed composed of a plurality of the formed spherical granular particles.

20 11. A method for manufacturing a bleach activator having alkyloxy compound, comprising:

(S1) mixing a plurality of fine powders composed of alkyloxy compound for bleaching activation expressed by the following Chemical Formula 1 with a water-soluble binder, and making the mixture into cylindrical granular particles having an average diameter of 0.1 to 3 mm and a length of 0.1 to 30 mm with the use of an extruder and a pelletizer;

25

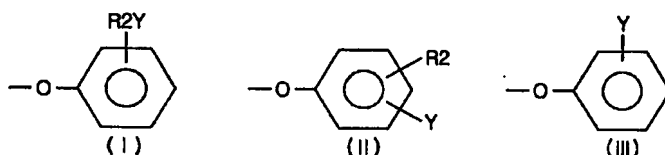
Chemical Formula 1



where  $R_1$  and  $R_3$  are respectively one selected from the group consisting of  
 5 alkyl, alkylene, aryl, alkaryl, and alkarylene, which have a carbon number of 1 to 20,  
 $n$  is an integer from 0 to 10, and  $L$  is a leaving group selected from the group  
 consisting of (I) to (III) of the following Chemical Formula 2:

Chemical Formula 2

10



where  $R_2$  is one of alkyl and alkylene, having a carbon number of 1 to 20,  $Y$   
 15 is one selected from the group consisting of hydrogen, chlorine, bromine,  $SO_3M$ ,  
 $CO_2M$  and  $OSO_2M$ , and  $M$  is one selected from the group consisting of hydrogen,  
 alkali metal ion, ammonium ion and equivalent alkaline earth metal; and

(S2) forming a cylindrical granular particle fluidized bed by putting  
 cylindrical granular particles into a predetermined container where a gas flows, and  
 20 then fluidizing the particles; and

(S3) forming a coating layer on a surface of the cylindrical granular particle  
 by spraying a solution containing a coating material to the cylindrical granular  
 particle fluidized bed.

25 12. A method for manufacturing a bleach activator having alkyloxy  
 compound according to claim 10 or 11,

wherein the water-soluble binder is at least one selected from the group

consisting of white sugar, glucose, starch, gelatin, polyethylene glycol, alkyl polyethoxylate, sorbitan fatty acid esters, linear alkylbenzene sulfonate, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, hydroxypropyl cellulose, arabic gum, ethyl cellulose and polyvinyl pyrrolidone.

5

13. A method for manufacturing a bleach activator having alkyloxy compound according to claim 10 or 11,

wherein the coating material is selected from the group consisting of inorganic substance, water-soluble organic substance, and their mixture.

10

14. A method for manufacturing a bleach activator having alkyloxy compound according to claim 13,

wherein the inorganic substance is at least one selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, sodium sulfate, zeolite, talc, clay, and silica; and wherein the water-soluble organic substance is at least one selected from the group consisting of polyethylene glycol, alkyl polyethoxylate, carboxy methyl cellulose, hydroxyethyl cellulose, methyl cellulose, hydroxypropyl cellulose, 2-methyl-5-vinylpyridine-methylacrylate-methacrylic acid polymer, and polyvinyl pyrrolidone.

20

15. A method for manufacturing a bleach activator having alkyloxy compound according to claim 10 or 11,

wherein the coating layer has a thickness of 1 to 100  $\mu\text{m}$ .

25

16. A bleach composition containing inorganic peroxide, which comprises 0.01 to 15 wt% of the alkyloxy bleach activator defined in any of the claims 1 to 9 on the basis of the weight of the entire composition.

17. A bleach composition according to claim 16,  
wherein the inorganic peroxide is selected from the group consisting of  
percarbonate salt, perborate salt and their mixture.

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2004/001146

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC7 C11D 3/395**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C11D, C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Korean Patents and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
cKIPASS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5705091 A (THE CLOROX COMPANY) 6 JANUARY 1998 Cited in the application, See the whole document	1-17
Y	US 5458801 A (KAO CORPORATION) 17 OCTOBER 1995 See column 2 line 23 - column 3 line 21, column 8 line 65 - column 11 line 49	1-17
A	US 6358902 B1 (THE PROCTER & GAMBLE COMPANY) 19 MARCH 2002 See column 5 line 36 - 48, claim 14	1,7,8,13,14,16,17
A	US 5534195 A (THE PROCTER & GAMBLE COMPANY) 9 JULY 1996 See column 10 line 18 - column 11 line 67	1,6-8, 12-14
A	US 6617300 B2 (THE PROCTER & GAMBLE COMPANY) 9 SEPTEMBER 2003 See column 13 line 48 - column 16 line 24	1,6-8, 12-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 JANUARY 2005 (14.01.2005)

Date of mailing of the international search report

**18 JANUARY 2005 (18.01.2005)**

Name and mailing address of the ISA/KR



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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

PCT/KR2004/001146

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5705091 A	06.01.1998.	None	
US 5458801 A	17.10.1995.	JP 2951767 B2 DE 4232494 A1	20.09.1999. 01.04.1993.
US 6358902 B1	19.03.2002.	WO 99/55818 A1 EP 1076684 A1 JP 2002-513072 T2 CN 1307629 T BR 9910030 A MA 24847 A1	04.11.1999. 21.02.2001. 08.05.2002. 08.08.2001. 26.12.2000. 31.12.1999.
US 5534195 A	09.07.1996.	EP 736086 A1	09.10.1996.
US 6617300 B2	09.09.2003.	None	